Synthesizing New Complexes Using [HPEBH=4-Hydroxy-N'-(1-(Pyridine-2-yl) ethylidene) Benzohydrazide)]

Hanin.AL-Hamoud
Master. student: Department of chemistry-Faculty of Science-Albaath university, SYRIA

Moudar M.AL-Khuder
Dr. for Inorganic Chemistry: Department of chemistry-Faculty of Science-Albaath University, SYRIA

Zohria.Salem
Dr. for Inorganic Chemistry: Department of chemistry-Faculty of Science-Albaath University, SYRIA

Abstract

In this study, a new ligand [HPEBH=4-Hydroxy-N'-(1-(Pyridine-2-yl) ethylidene) Benzohydrazide)], and it's transition metal complexes with [Ni^{II}, Co^{II}, and Cu^{II}] were synthesized.The synthesis of ligand (HPEBH) was carried by the condensation of 1-(Pyridine-2-yl)ethan-1-one with 4-HydroxyBenzohydrazone .Then, the reaction of this ligand with Cobalt (II), Nickel (II), Copper (II) ions were carried out using metal chloride salt by the (2:1) molar ratio, fowr new mononuclear. complexes were obtained which have the formula [$M(HPEBH)_2$] ; M= Ni^{II} , Co^{II}, Cu^{II} The structures of the ligand and it's complexes were elucidated by FT-IR , U.V.–visible .

Keywords: hydrazone, azometine, pyridine, metal complexes.

1. Introduction

Hydrazones are present in many of the bioactive heterocyclic compounds that are of wide interest because of their diverse biological and clinical applications. This created interest in researchers who have synthesized variety of hydrazone derivatives and screened them for their various biological activities viz. anticonvulsant, antidepressant, analgesic, anti-inflammatory, antiplatelet, antimalarial, antimicrobial, antimycobacterial, anticancer, vasodialator, antiviral, antischistosomiasis, anti-HIV, anthelmintic, antidiabetic and trypanocidal activities. Hydrazones possessing an azometine –NHN=CH– proton constitute an important class of compounds as target structures and evaluated their biological activities. These observations have been guiding for the development of new hydrazones that possess varied biological activities. Which has shown us the importance of synthesizing complexes containing hydrazone derivatives that can form stable metal complexes with most transition metals [1].

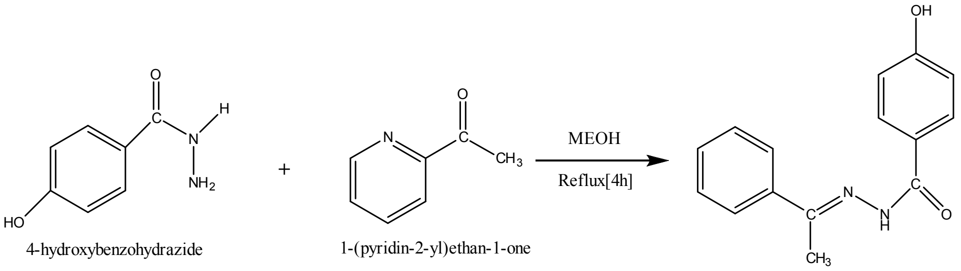
2. The Objective of the Research:

- T0 prepare 4-hydroxy-N' -(1- (Pyridine-2-yl) ethylidene) Benzohydrazide) and confirm the identity of the product spectroscopy (IR spectrum) and UV spectroscopy (U.V-visible).
- To study the possibility of forming complexes with some of the transition metal salts.

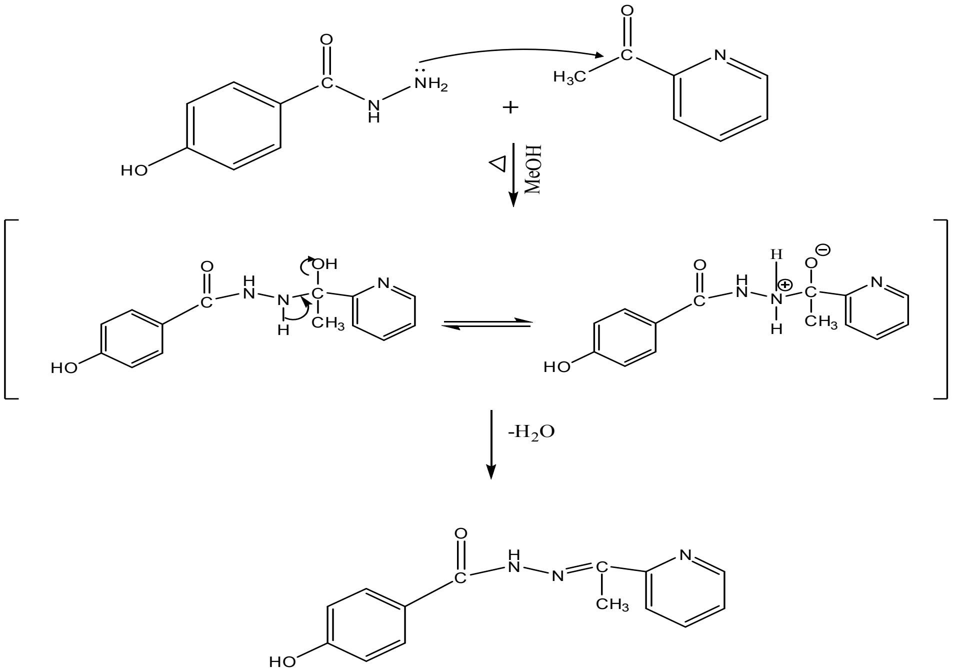
3. Results and discussion:

1-3- Preparation of 4- hydroxy -N'-(1-(Pyridine-2-yl))Binzohydrazide =(HPEBH):

The preparation of the condensation of 1- (pyridine-2-yl) ethan-1-one with 4-hydroxybenzohydrone in absolute methanol as solvent and reflux for 4 hours was done according to the following reaction:



A preparation reaction associated with HPEBH is one of Schiff's methods of preparation.
The Interaction occurs via adding and eliminating an interaction between
1-pyridine-2-yl (ethan-1-one) and 4- hydroxyBenzohydrazone.it occurs through two phases **[2]**:
Phase 1: The interaction of the nucleophilic addition of the free electronic pair found in the nitrogen atom of the hydrazine to the carbonyl group carbon to give an unstable intermediate compound (carbinolamine).
Phase 2: Dehydration interaction of the water molecule and formation of the amine bond, according to the following proposed mechanism:



In the IR spectra of the ligands(Figure 1), The stretching vibration of the NH group is observed at 3203cm^{-1} .The characteristic amide I [νC=O] band appears at 1649 cm^{-1} . The stretching vibration of the C=Nimine and C=Npyridine is observed at 1607, 1578 cm^{-1}, respectively. The broad medium intensity band appearing at 3397 cm^{-1} is assigned to the characteristic OH absorptions.The stretching vibration of the C-Npyridine and (N-N) is observed at 1374, 1133 cm^{-1}, respectively.

This can be seen through the published studies and researches in this scientific field of study **[3]**.

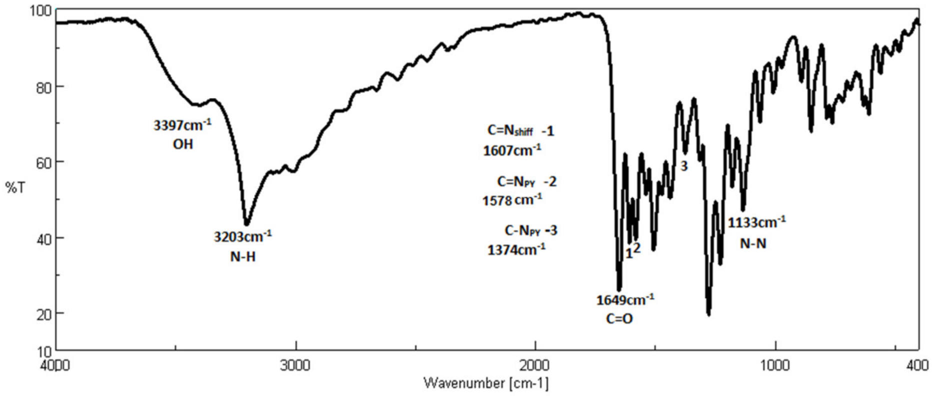


Fig. 1: IR spectrum of HPEBH ligand

Electronic spectra (UV-visible) of the ligand (HPEBH) was achieved in Methanol solution. The appearance of two bands in the electronic spectra (Fig 2), in the regions (220, 280 nm).The first on site(220 nm) absorption 0f the electronic transmission of

($\pi \rightarrow \pi^*$) is due to containing the ligand on binary bonds such as the group of azomethane (C = N) and the group of (C = N) pyridine and (C=C) of the aromatic ring. The second on-site (280 nm) absorption is due to electronic transmission of ($n \rightarrow \pi^*$) type due to the presence of non-nitrogen-bonded nitrogen pairs of the NH group and the carbon atom of the carbonyl group [2].

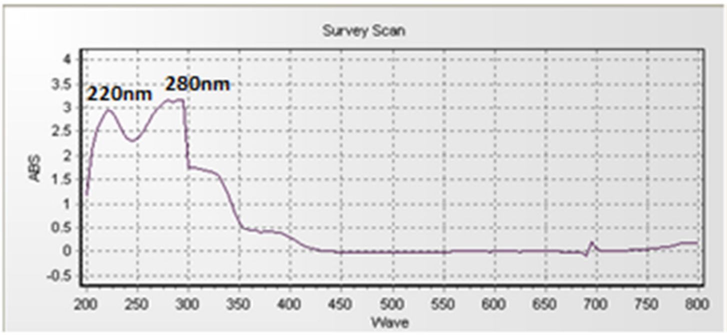
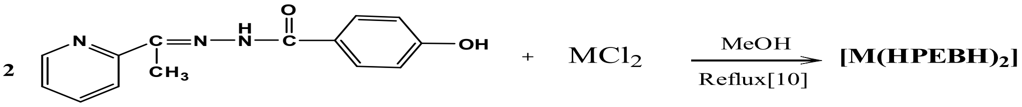


Figure 2: Electronic absorption spectra of ligand (HPEBH)

Thus, the ligand HPEBH was confirmed by using IR spectroscopy and UV-VIS spectroscopy.

2.3. Preparation of Complexes using Ligand (HPEBH):

After confirming the structure of the artificially ligand (HPEBH), it was reacted with the general form of MCl_2 ($M = Ni^{II}$, Co^{II}, Cu^{II}) in order to form metal complexes according to the following reaction:



$M=Ni^{II},Co^{II},Cu^{II}$

Some physical properties of both the HPPEBH and its metal complexes were calculated and the ratio of the metal ratio in the complexes was measured by the incineration method as shown in Table **(1)**.

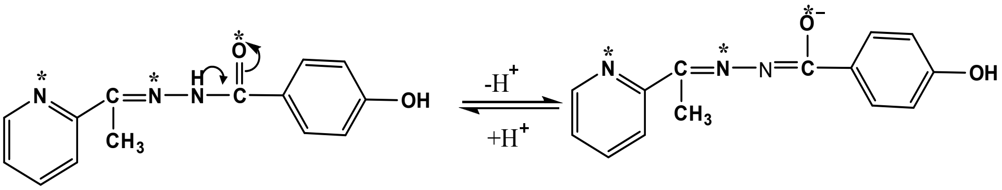
Table (1): Physical properties
(HPEBH), its mineral complexes and the ratio of metal in the complex

Comp.	Formulas (MW)	Color	M.p (oC)	Yield (%)	Metal ratio	
					Calculated %	(Found) %
HPEBH	**C14H13N3O2 (255g.mol-1)**	**white**	**180**	**72.24**	**------**	**------**
[Ni(HPEBH)2]	**C28H24N6O4Ni (566,71g.mol-1)**	**Light Green**	**260**	**28.73**	**10,35**	**8,468**
[Co(HPEBH)2]	**C28H24N6O4Co (566,9g.mol-1)**	**Brown**	**265**	**32.68**	**10,39**	**10,408**
[Cu(HPEBH)2]	**C28H24N6O4Cu (571,546g.mol-1)**	**Green**	**246**	**41.16**	**11,118**	**11,48**

From the data in Table **(1)** , the ratio of the calculated and calculated metal is theoretically consistent with the proposed molecular formulas.

The FT-IR spectra and the UV-Visible spectra of the complexes were also studied as follows:

The infrared absorption bands of the complexes (Fig. 3-5) are given and assigned in Table **2** .The IR spectra of the complexes show significant differences from the free ligand. The bands due to C=N imine, ν(C=O) and amide ν(NH) are absent in the IR spectra of the complexes. But a new band appears at (1334-1321cm^{-1}) .It is probably due to C-O stretching. The NH proton is likely lost via deprotonation. The resulting enolic oxygen and the azomethine nitrogen takes place in coordination.



The shift of ν(N-N) stretch of the complexes to higher energy by 1174-1168 cm^{-1} compared to that of free ligand can be another evidence for the involvement of azomethine nitrogen in coordination, whereas (C=N)pyridine absorptions are moved to (1572-1567cm^{-1}).One new band probably appears in 1597-1594 cm^{-1}; due to C=N-N=C stretching.

According to IR data and stoichiometry of these complexes, the ligand acts as a neutral O,N,N-tridentate and proposed to be six-coordination with a N4O2 donor environment. Each of ligand is coordinated through the pyridine nitrogen, the imine nitrogen and the carbonyl oxygen **[3]**.

Table 2: IR spectral data of the ligand(HPEBH) and their metal complexes (cm^{-1})

Comp.	ν(OH)	ν(NH)	ν(C=O)	ν(C=N) imine	ν(C=N) Pyridine	ν(C-N) Pyridine	(C-N) ألكيل	ν(N-N)	C=N-N=C	C-O
(HPEBH)	3397	3203	1649	1607	1578	1374	1314	1133	----	----
[Ni(HPEBH)2]	3423	----	----	----	1569	1377	----	1168	1594	1321
[Co(HPEBH)2]	3424	----	----	----	1567	1376	----	1169	1597	1327
[Cu(HPEBH)2]	3406	----	----	----	1572	1378	----	1174	1597	1334

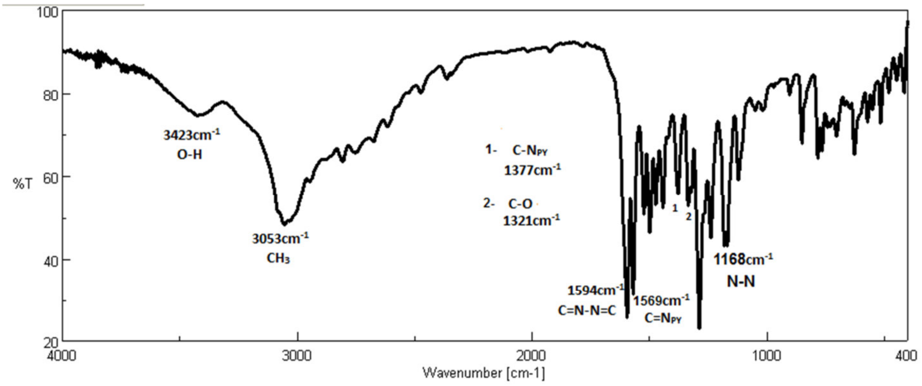


Fig. 3: IR spectrum of [Ni(HPEBH)$_2$] complex

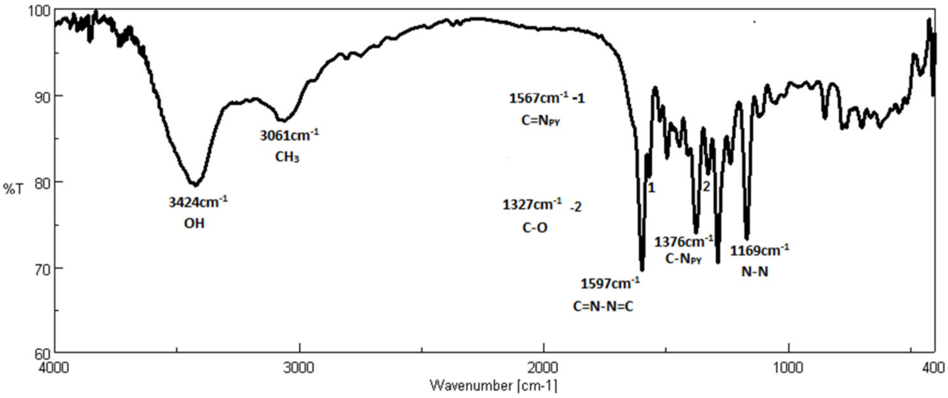


Fig. 4: IR spectrum of [Co(HPEBH)$_2$] complex

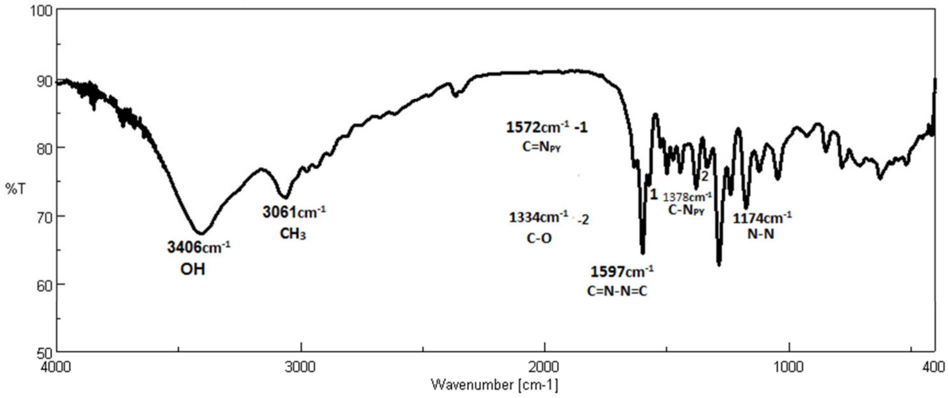


Fig. 5: IR spectrum of [Cu(HPEBH)$_2$] complex

Electronic spectra(UV-visible) of the metal(II) complexes was achieved in Methanol solution (Fig. 7-9). It has been observed through the shifts in the location of these beams which occurred from those associated with the free ligand(HPEBH),confirming the support between the bond and the metal ion ,adding to The appearance of new one band in the electronic spectra of complexes in the regions (390-400 nm) .It may be assigned to the transmission of charge from (MLTC) as a result of granting free electronic pairs of metal ion to the ligand (M→ L)**[2]** .

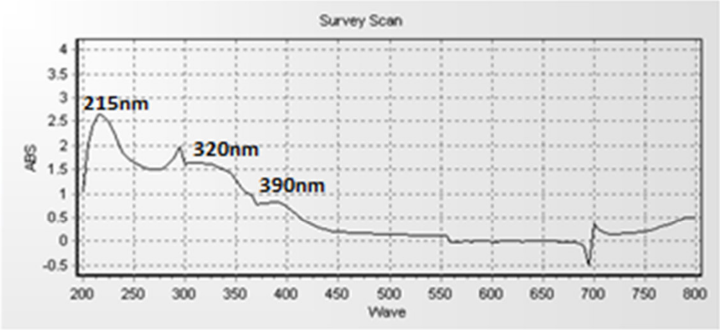


Figure7: Electronic absorption spectra of complex [Ni(HPEBH)$_2$]

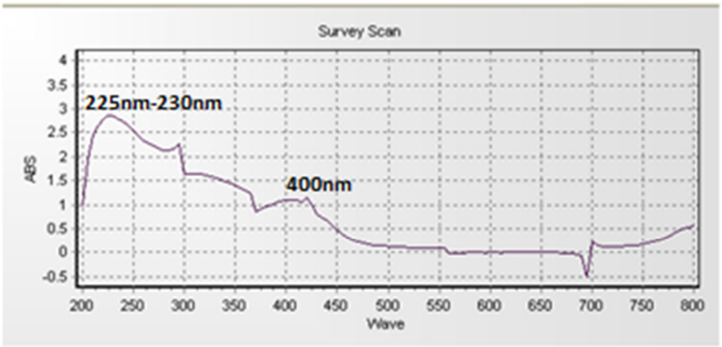


Figure8: Electronic absorption spectra of complex [Co(HPEBH)$_2$]

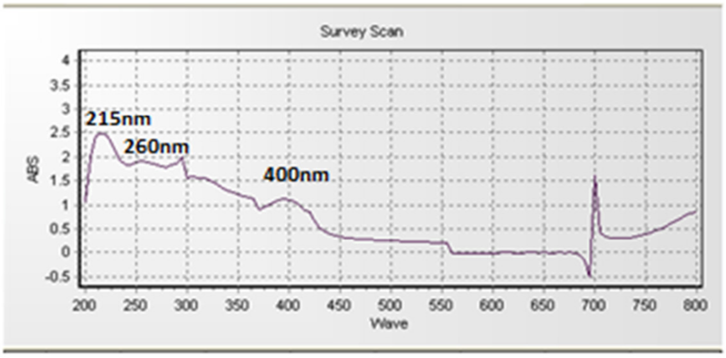


Figure9: Electronic absorption spectra of complex [Cu(HPEBH)$_2$]

3.3. Detection of chlorine content in mineral complexes:

First, the electrical conductivity of complex solutions was measured(in methanol solvent) and the electrical conductivity was 30.2 ,26.1 , 86.5 For Cobalt, Copper and Nickel alloys respectively. This indicates that they are non-electrolytic. There is no chlorine ion in the outer ball.

The chlorine content in the inner ball of the mineral concentrates was determined by the following method:

We add 0.1 g of the prepared metal complex to an appropriate amount of concentrated acid to break the organic compounds, heat the mixture until dissolved. The solution becomes clear,and we add the silver nitrate solution**[2]**.It was observed that no white precipitation is present in the Nickel, Cobalt and Copper complexes There is no chlorine ion in the internal ball for metal complex.

As a result of what has been mentioned above, and based on the previous apectral study and the physical properties of the prepared complexes, we suggest the general molecular formula of [M(HPEBH)$_2$] when [M=Ni^{II} , Cu^{II} ,Co^{II}] are all stable and constant in the air. The vacuum structure is as follows:

4. Experimental

4.1 Devices and chemicals used:

-Infrared spectrometer (FT-IR)
Jascow - Infrared Spectrophotometer Fourier Transform
FT/IR-spectrum-4100 (KBr).
-Ultraviolet spectrometer
Jascow - (UV-Visible) Spectrophotometer
(UV-Visible) / V-350
-Fusion degree device Electrothermal Melting Point
Apparatus
-Balance sensitive type Sartorius BL-210S
- A heater with a magnetic motor Agimatic P-Selecta 243
- The chemicals used were prodused by the company :
Aldrich-sigma.
It has been used directly without recrystallization.

4.2. Syntheses of (HPEBH) =4-hydroxy-N'-(1-(Pyridine-2-yl)ethylidene)Binzohydrazide):

To a 30 ml methanol solution of Methyl-2-Pyridyl keton (1.14 ml , 10 mmol), 4-hydroxy benzohydrazide (1.52g, 10mmole) in 50 ml methanol was added and the reaction mixture was stirred while refluxing for 4h. On reducing the volume to ∼30 ml. The resultant solid was filtered and thoroughly washed with ethanol (2 × 5 ml) followed by diethyl ether (2 × 5 ml). The solid was recrystallised from hot ethanol.

4.3 Syntheses of the complexes:

All the complexes were prepared following a similar method of reacting a methanol solution of the metal salt, ligand in a 1:2 ratio. Preparation of one of the complexes is described below .

To a 50 ml methanol solution of the (HPEBH) ligand (1 mmol) . MCl_2 anhydrous (0.5 mmol) when [$M = Co^{II}$, Ni^{II}, Cu^{II}] in 20 ml methanol was dded and the reaction mixture was stirred while refluxing for 7h(T=65^{o}c) colored solution was changed immediately . After 7 h the volume of the solution was reduced to ∼30 ml and filtered. The resultant solid was obtained and washed with methanol (3 × 3 ml), followed by diethyl ether (2 × 5 ml).

References

[1]. Negi. V. J, Sharma. A. K, Negi. J. S, Ram. V, BIOLOGICAL ACTIVITIES OF HYDRAZONE DERIVATIVES IN THE NEW MILLENNIUM, International Journal of Pharmaceutical Chemistry 2012; vol 2: pp 100-129

[2]. AL-Noaymi. M. M, AL-Khuder. M. M, Abaas. G, Synthesis and Spectral Study of 1,4-Diformylbenzenebishydrazone Ligand and Their Complexes with Some Transition Metal (II). Journal of Albaath University 2012; vol 33: pp 124-105.

[3]. AL-Ne'aimi. M. M, Synthesis and characterization of bis-acylhydrazone derivatives as tetradentate ligands and their dinuclear metal(II) complexes, Chemical Engineering 2012, vol 56\5, pp 83-90.